Taylor Dispersion with Adsorption and Desorption

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We use a stochastic approach to show how Taylor dispersion is affected by kinetic processes of adsorption and desorption onto surfaces. A general theory is developed, from which we derive explicitly the dispersion coefficients of canonical examples like Poiseuille flows in planar and cylindrical geometries, both in constant and sinusoidal velocity fields. These results open the way for the measurement of adsorption and desorption rate constants using stationary flows and molecular sorting using the stochastic resonance of the adsorption and desorption processes with the oscillatory velocity field.

I. INTRODUCTION

In presence of a uniaxial stationary laminar fluid flow, the diffusion of Brownian particles along the direction of the flow is enhanced by an amount proportional to the inverse of the molecular diffusion coefficient D_b. This effect, known as Taylor dispersion [1, 2], originates from the combination of the inhomogeneous velocity field experienced by the particles and the diffusive transverse motion which leads to a random sampling of these fast and slow streamlines. Taylor dispersion has implications in many fields, especially those involving chemical reactions and determination of reaction rates such as microfluidics and chromatography, and has thus been the subject of a number of works both at the theoretical and experimental level [3–8]. In numerous practical situations, Taylor dispersion in the bulk flow is coupled to the adsorption and desorption processes taking place at the walls confining the fluid. So far, the theoretical analysis of the resulting process has mainly been done explicitly in two limiting situations.

In the first class of models, the transverse motion is not explicitly considered, which physically corresponds to the infinitely well stirred limit of high diffusion coefficient D_b. A representative example is the famous two-state model of chromatography introduced by Giddings and Eyring in 1955, in which a particle can be either in the mobile phase (in the flow) or in the immobile phase (adsorbed on the confining walls), the rates of change between phases being constant [9]. An important extension concerns the case when the velocity of the mobile phase oscillates with time according to $v \cos(\omega t)$ [10, 11]. In particular, stochastic resonance has been shown to occur if the rates of change between phases are both equal to $\omega/2$, leading to a maximum of the dispersion coefficient [12, 13]. This effect has recently proved to have applications in molecular sorting [14, 15].

The second class of models has investigated explicitly the transverse motion, but for specific kinetics of adsorption and desorption: In [16], the dispersion coefficient is calculated when the exchanges with the surface are infinitely fast (local chemical equilibrium), while Biswas and Sen have considered the situation of irreversible adsorption on the surface [17]. Besides, these studies focus on stationary velocity fields and the important case of oscillating velocity fields mentioned above is not considered.

In this article, we develop a theoretical analysis of Taylor dispersion in presence of general adsorption and desorption processes. Relying on a stochastic approach (i) we derive explicit expressions of the dispersion coefficient for the canonical examples of Poiseuille flows in planar and cylindrical geometries, both for stationary and oscillating velocity fields, thus opening the way to the determination of heterogeneous rate constants from the mean velocity and dispersion coefficient; (ii) we recover the fact that, in the case of a stationary velocity field, the sources of dispersion associated to bulk transport and adsorption and desorption processes combine additively [18, 19]; (iii) in the case of an oscillatory velocity field, we show that the dispersion coefficient can be optimized and discuss possible implications in the context of molecular sorting.

II. THE MODEL

We consider a Brownian particle in a flow of velocity field v in direction x. The position of the particle in the transverse direction is denoted by $\mathbf{y}$ and the full position by $\mathbf{r} \equiv (x, \mathbf{y})$. The longitudinal dynamics of the particle is assumed to be given by the Langevin equation:

$$\dot{x}(t) = v(\mathbf{y}(t), t) + \mathbf{1}_b(\mathbf{y}(t))\eta_b(t) + \mathbf{1}_s(\mathbf{y}(t))\eta_s(t), \quad (1)$$

where $\mathbf{1}_b(\mathbf{y}(t))$ stands for the indicator function of the bulk b (equal to 1 if the particle's position is in the bulk and 0 otherwise) which accounts for bulk diffusion (with diffusion coefficient D_b) and $\mathbf{1}_s(\mathbf{y}(t))$ for the indicator function of the surface s associated to surface diffusion

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(with diffusion coefficient D_s). The independent Gaussian white noises η_b and η_s are defined by their correlation functions:

$$\begin{cases} \langle \eta_b(t) \rangle = \langle \eta_b(t) \rangle = 0 \\ \langle \eta_b(t)\eta_b(t') \rangle = 2D_b\delta(t-t') \\ \langle \eta_s(t)\eta_s(t') \rangle = 2D_s\delta(t-t'). \end{cases} \quad (2)$$

The transverse diffusion equation is driven by the evolution equation:

$$\begin{cases} \partial_t P(\mathbf{y},t|\mathbf{y}',0) = D_b\nabla^2 P(\mathbf{y},t|\mathbf{y}',0), \forall \mathbf{y} \in b \\ \partial_t \Gamma(\mathbf{y},t|\mathbf{y}',0) = -k_d\Gamma(\mathbf{y},t|\mathbf{y}',0) + k_a P(\mathbf{y},t|\mathbf{y}',0) \\ \qquad = D_b\partial_n P(\mathbf{y},t|\mathbf{y}',0), \forall \mathbf{y} \in s \end{cases}$$
$$(3)$$

where k_a (resp. k_d) is the adsorption (desorption) rate in length·time^{-1} (resp. time^{-1}) [20], P (resp. Γ) is the propagator corresponding to a final state in the bulk (resp. on the surface) and ∂_n stands for the normal derivative. Initially, the particle is assumed to start from $x = 0$ and the process $\mathbf{y}(t)$ to be stationary, characterized by the stationary distribution $P_{stat}(\mathbf{y})$ (uniform within each phase and depending only on the ratio k_a/k_dL) and the transition probability $P(\mathbf{y},t|\mathbf{y}',t') \equiv P(\mathbf{y},t-t'|\mathbf{y}',0)$.

The first two moments of $x(t)$ are then respectively found from Eqs.(1), (2) to be given by

$$\langle x(t) \rangle = \int_0^t dt' \int_b d\mathbf{y} P_{stat}(\mathbf{y})v(\mathbf{y},t') \quad (4)$$

where the integration domain of the spatial integral is the transverse cross section in the bulk b and

$$\langle x^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle v(\mathbf{y}(t'),t')v(\mathbf{y}(t''),t'') \rangle$$
$$+ 2D_b\langle T_b(t) \rangle + 2D_s\langle T_s(t) \rangle, \quad (5)$$

where $T_b(t)$ (resp. $T_s(t)$) is the cumulative time spent in the bulk (on the surface) up to time t. Finally, one has

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 - 2D_b\langle T_b(t) \rangle - 2D_s\langle T_s(t) \rangle =$$
$$2\int_0^t d\tau \int_\tau^t dt' \int_b d\mathbf{y_1} \int_b d\mathbf{y_2} v(\mathbf{y_1},t')v(\mathbf{y_2},t'-\tau) \times$$
$$\times P_{stat}(\mathbf{y_2})\left[P(\mathbf{y_1},\tau|\mathbf{y_2},0) - P_{stat}(\mathbf{y_1})\right] \equiv f(t). \quad (6)$$

We now specialize this general formula to the two experimentally relevant cases of either a stationary or sinusoidal velocity field.

III. CASE OF A STATIONARY VELOCITY FIELD

In the case of a stationary velocity field $v(\mathbf{y},t) \equiv v(\mathbf{y})$, the large time limit of the variance of the displacement is easily shown from Eq. (6) to be given by

$$\langle x^2(t) \rangle - \langle x(t) \rangle^2 \underset{t\to\infty}{\sim} 2Kt, \quad (7)$$

where the dispersion coefficient is $K = P_{stat}(b)D_b + P_{stat}(s)D_s + K_v$, where $P_{stat}(b)$ (resp. $P_{stat}(s)$) is the stationary probability to be in the bulk (resp. to be adsorbed on the surface) and the velocity-dependent part reads:

$$K_v = \int_b d\mathbf{y_1} \int_b d\mathbf{y_2} v(\mathbf{y_1})v(\mathbf{y_2})P_{stat}(\mathbf{y_2})h(\mathbf{y_1}|\mathbf{y_2}), \quad (8)$$

with

$$h(\mathbf{y_1}|\mathbf{y_2}) \equiv \int_0^\infty \left[P(\mathbf{y_1},t|\mathbf{y_2},0) - P_{stat}(\mathbf{y_1})\right] dt. \quad (9)$$

Note that $h(\mathbf{y_1}|\mathbf{y_2})$ is the pseudo-Green function [21] of the transverse problem, which satisfies $-D_b\nabla^2 h(\mathbf{y_1},\mathbf{y_2}) = \delta(\mathbf{y_1}-\mathbf{y_2}) - P_{stat}(\mathbf{y_1})$. As soon as this pseudo-Green function can be determined, Eq. (8) provides a general expression of the Taylor dispersion coefficient in presence of adsorption and desorption processes.

Importantly, this expression can be made fully explicit in the canonical examples of planar and cylindrical Poiseuille flows, corresponding respectively to velocity fields $v(y) = 6\bar{v}\frac{y}{L}\left(1 - \frac{y}{L}\right)$ (the transverse cross section being a segment of length L and $y \in [0,L]$) and $v(r,\theta) \equiv v(r) = 2\bar{v}\left(1 - \frac{r^2}{R^2}\right)$ (the transverse cross section being a disk of radius R and $\mathbf{y} = (r,\theta) \in [0,R] \times [0,2\pi]$), where $\bar{v}$ stands for the velocity averaged over a cross section. The explicit determination of the pseudo-Green function $h(\mathbf{y_1}|\mathbf{y_2})$ is conveniently performed by first Laplace transforming Eq.(3), calculating the Laplace transform of the propagator and then going to the small Laplace variable limit. Note in particular that the boundary conditions Eq.(3) associated to adsorption/desorption become simple radiative boundary conditions in the Laplace domain (see for example ref. [22]). Lengthy but straightforward calculations finally lead to symmetrical functions of their arguments, which read

$$h^{\text{plan.}}(y_1|y_2) = \frac{\frac{1}{2}y_1^2 + \frac{k_a}{k_d}y_1 + \frac{1}{2}y_2^2 - y_2\left(L + \frac{k_a}{k_d}\right)}{D_b\left(L + \frac{2k_a}{k_d}\right)}$$
$$+ \frac{\frac{1}{3}L^3 + \frac{2D_bk_a}{k_d^2} + \frac{k_aL^2}{k_d} + \frac{Lk_a^2}{k_d^2}}{D_b\left(L + \frac{2k_a}{k_d}\right)^2}$$
$$(10)$$

if $y_1 < y_2$ and

$$\frac{1}{2\pi}\int_0^{2\pi} d\theta_2 h^{\text{cyl.}}(r_1,\theta_1|r_2,\theta_2) = \frac{1}{2\pi D_b}\ln\frac{R}{r_2}$$
$$+ \frac{\left(2R + 4\frac{k_a}{k_d}\right)(r_1^2 + r_2^2) - 3R^3 + 16\frac{D_bk_a}{k_d^2}}{8\pi R D_b\left(R + 2\frac{k_a}{k_d}\right)^2}$$
$$(11)$$

if $r_1 < r_2$. The velocity-dependent part of the dispersion coefficients is then found to have the same form in both geometries:

$$K_v^{\text{Pois.}} = \alpha \frac{l^2 \bar{v}^2}{D_b} \frac{\beta l \left(\frac{k_a}{k_d}\right)^2 + \gamma l^2 \frac{k_a}{k_d} + l^3}{\left(l + 2\frac{k_a}{k_d}\right)^3} + \frac{\bar{v}^2}{k_d} \frac{2l^2 \frac{k_a}{k_d}}{\left(l + 2\frac{k_a}{k_d}\right)^3} \tag{12}$$

where the length l and constants (α, β, γ) are to be substituted by L and $(\frac{1}{210}, 102, 18)$ in the planar case and R and $(\frac{1}{48}, 44, 12)$ in the cylindrical one.

A few comments are in order. (i) The specific case of infinitely fast exchange with the surface (local chemical equilibrium), considered in the cylindrical case in [16] as one of the generalizations of Taylor dispersion, is recovered in the joint limit $k_a \to \infty$, $k_d \to \infty$ with $k_a/k_d L$ fixed, and is given by the first term of the right hand side (r.h.s.) of the general expression (12). (ii) In the infinitely well stirred limit $D_b \to \infty$, $K_v^{\text{Pois.}}$ is reduced to the second term of the r.h.s. of Eq. (12). This second source of dispersion, associated to adsorption and desorption kinetics only, corresponds to the 0-dimensional dispersion coefficient used in the usual two-state model of chromatography [12], with a rate $2k_a/l$ ($l = L, R$) for the transition from mobile to immobile states. (iii) Note that these two contributions to dispersion turn out to combine themselves additively. (iv) The knowledge of the mean displacement $\langle x(t) \rangle \sim P_{stat}(b)\bar{v}t$ (see Eq. (4)) and the dispersion coefficient Eq. (12) enables the experimental determination of k_a and k_d from the measurement of the average velocity and dispersion coefficient for a given species interacting with a given surface. (v) It also allows to design a chromatographic column for the separation of a mixture with known adsorption and desorption rates. However, in the important case where the components of the mixture have different kinetic rates k_a and k_d but

similar partitioning coefficients $k_a/k_d L$, such a separation is impossible with a stationary flow, since $P_{stat}(b)$, hence $\langle x(t) \rangle$, of all species are similar. As we now proceed to show, efficient sorting can nevertheless be achieved in this case by resorting to an oscillatory flow and exploiting the stochastic resonance between the exchange kinetics and the flow, thereby extending the idea put forward by Alcor *et al.* in another context [14, 15].

IV. CASE OF A SINUSOIDAL VELOCITY FIELD

We now consider the case where the velocity field is a sinusoidal function of time $v(\mathbf{y}, t) \equiv v(\mathbf{y}) \cos(\omega t)$. In this case, the average position $\langle x(t) \rangle$ tends to 0 at long time, while the function $f(t)$ in Eq. (6) becomes:

$$f(t) = \int_0^t d\tau \int_\tau^t dt' \int_b d\mathbf{y_1} \int_b d\mathbf{y_2} v(\mathbf{y_1}) v(\mathbf{y_2}) P_{stat}(\mathbf{y_2}) \times$$
$$\times \left[P(\mathbf{y_1}, \tau | \mathbf{y_2}, 0) - P_{stat}(\mathbf{y_1}) \right] \left[\cos\omega(2t' - \tau) + \cos\omega\tau \right]. \tag{13}$$

In the large time limit, the term in $\cos\omega(2t' - \tau)$ becomes negligible and the velocity-dependent part of the dispersion coefficient is given by

$$K_v = \frac{1}{2} \int_b d\mathbf{y_1} \int_b d\mathbf{y_2} v(\mathbf{y_1}) v(\mathbf{y_2}) \times$$
$$\times P_{stat}(\mathbf{y_2}) Re(\widehat{P}(\mathbf{y_1}, -i\omega | \mathbf{y_2})), \tag{14}$$

where $Re(\widehat{P}(\mathbf{y_1}, -i\omega | \mathbf{y_2}))$ stands for the real part of the Laplace transform of the propagator, with the Laplace variable $s \equiv -i\omega$. We focus here on the canonical case of the planar Poiseuille flow described above. The final result for the velocity-dependent part of the dispersion coefficient reads:

$$K_v^{\text{Pois.}} = \frac{L^2 \bar{v}^2}{D_b} \frac{3Z}{2X^6(2Y + Z)} \frac{\chi_c^+ \cosh X + \chi_c^- \cos X + \chi_s^+ \sinh X + \chi_s^- \sin X}{\rho_c^+ \cosh X + \rho_c^- \cos X + \rho_s^+ \sinh X + \rho_s^- \sin X} \tag{15}$$

where we have introduced the polynomials

$$\begin{cases} \chi_c^\pm = 2X^4 Y^2 - 6X^2 Y \pm (X^2 Z^2 + X^2 - 12Y) \\ \chi_s^\pm = 2X^3 YZ + 12XY \pm (2X^3 Y - 12XY^2 - 3XZ^2 - 12XYZ - 3X) \\ \rho_c^\pm = 2X^2 Y^2 \pm (Z^2 + 1) \\ \rho_s^\pm = 2XYZ \pm 2XY \end{cases} \tag{16}$$

and the reduced variables $X \equiv L\sqrt{\omega/2D_b}$, $Y \equiv k_a/\omega L$ and $Z \equiv k_d/\omega$. This expression constitutes one of the main results of the present work. It extends in particular the results known in absence of adsorption and desorption at the wall [12] (recovered in the limits $Y \to 0$ or $Z \to \infty$) and in the case of an infinitely well stirred limit

in the transverse direction (corresponding to $X \to 0$) [10, 12, 14, 15], with an adsorption rate $2k_a/L$.

Besides being an important theoretical result in itself, the expression (15) also allows one to discuss the possibility of sorting components of a mixture in an oscillatory flow, in presence of adsorption and desorption processes.

Alcor *et al.*[14, 15] have demonstrated, both theoretically and experimentally, that an oscillatory driving (by an electric field) can be exploited to separate components of a mixture that switch between two bulk states with different rates. Using the 0-dimensional two-state model generally considered in chromatography, they showed that the dispersion coefficient displays in this case a maximum when the two rates are close to $\omega/2$, *i.e.* when the average time spent in each state are equal and comparable to a half-period of the driving, resulting in an effective rectification of the flow experienced by the particles. We now discuss the possibility of extending this idea to the case of Taylor dispersion with adsorption and desorption.
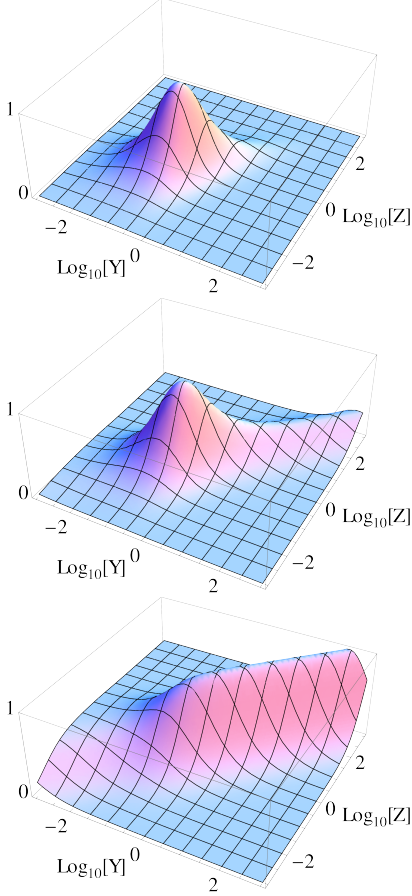

FIG. 1. (Color online) Velocity-dependent part K_v of the dispersion coefficient, normalized by the value at the optimum K_v^{opt} as a function of the reduced rates $Y = k_a/\omega L$ and $Z = k_d/\omega$, for three values of $X = L\sqrt{\omega/2D_b}$: 0, 1 and 3.5.

Importantly, we find that Taylor dispersion with adsorption and desorption at the walls of the confining surfaces also exhibits a stochastic resonance. However, the picture is more complex due to the coupling between motion in the direction transverse to the flow and the exchange processes. Indeed, $K_v^{\mathrm{Pois.}}(\omega)$ displays a global maximum for a set of finite reaction rates (k_a, k_d), provided that $X < X^* \approx 3.5$, as can be seen in Figure 1, which reports K_v normalized by the value at the opti-

mum K_v^{opt}. The optimal rates satisfy:

$$k_a^{\mathrm{opt}} = \omega L Y^{\mathrm{opt}}(X) \ \text{ and } \ k_d^{\mathrm{opt}} = \omega Z^{\mathrm{opt}}(X) \qquad (17)$$

where Y^{opt} and Z^{opt}, reported in Figure 2a, are well approximated by their small X expansions for an appreciable range (see Figure 2):

$$Y^{\mathrm{opt}} = \frac{1}{4} + \frac{11}{336}X^2 + \frac{163}{50400}X^4 + \frac{331}{1241856}X^6 + \mathcal{O}(X^8) \tag{18}$$

and

$$Z^{\mathrm{opt}} = \frac{1}{2} + \frac{71}{840}X^2 + \frac{17}{1800}X^4 + \frac{25427}{25872000}X^6 + \mathcal{O}(X^8), \tag{19}$$

and correspond to the following expansion of the optimal dispersion coefficient:

$$K_v^{\mathrm{opt}}(X) = \frac{L^2\bar{v}^2}{D_b}\left(\frac{1}{32X^2} + \frac{11}{3360} - \frac{79X^2}{564480} + \mathcal{O}(X^4)\right). \tag{20}$$
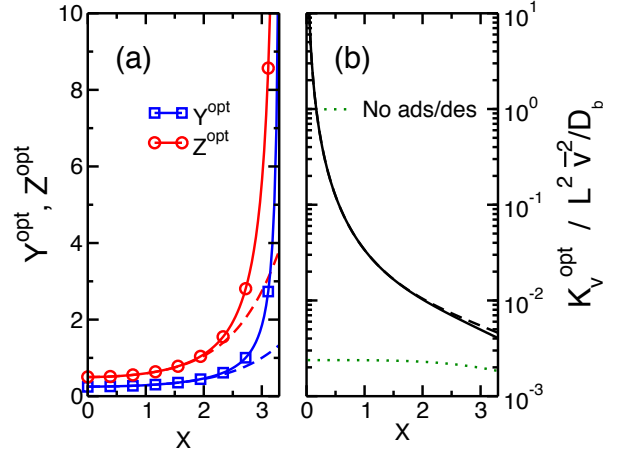

FIG. 2. (Color online) (a) Optimal reduced rates, $Y^{\mathrm{opt}} = k_a^{\mathrm{opt}}/\omega L$ and $Z^{\mathrm{opt}} = k_d^{\mathrm{opt}}/\omega$ as a function of $X = L\sqrt{\omega/2D_b}$ maximizing the velocity-dependent part of the dispersion coefficient K_v. (b) Corresponding values of the optimum K_v^{opt}, in units of $L^2\bar{v}^2/D_b$. Numerical results (solid lines) are compared to the analytical expressions Eqs. (18)-(20) for small X (dashed lines). In (b), K_v in the absence of adsorption and desorption is also indicated (dotted line).

While for small values of X, the resonance is obtained for $k_d \sim 2k_a/L \sim \omega/2$ and has similarities with the case of Alcor *et al.* [14, 15], the optimal rates can in fact differ by orders of magnitude from ω as $X \to X^*$. Moreover, while the resonance process is rather selective in the small X regime, as K_v decreases rapidly around the optimum, Figure 1 indicates that the selectivity deteriorates when X increases. Finally, the optimal dispersion coefficient, enhanced by orders of magnitude by adsorption and desorption at the walls, also decreases with increasing flow frequency (see Figure 2b). All these observations reflect the transition from the well-stirred regime $X \to 0$

where "chemical" and Taylor dispersions combine additively (the first two terms in Eq. (20) are proportional to $\bar{v}^2/k_d^{\mathrm{opt}}$ and $\bar{v}^2 L^2/D_b$, respectively), as in the stationary case, to one where exchange at the walls can be limited by the diffusive influx of mobile species. In the latter case, only a fraction of mobile species can benefit from the rectification mechanism allowed by the adsorption and desorption processes. Its effect on dispersion is then maximal when the particles spend the same time at the surface and in this boundary layer accessible by diffusion within a flow period (now regardless of reaction rates provided that the exchange is fast compared to the flow frequency).

V. DISCUSSION

This optimization of the dispersion coefficient can be used in the context of molecular sorting, where the problem is to isolate a species of given (k_a, k_d) from a mixture. In fact, the ratio $Z^{\mathrm{opt}}/Y^{\mathrm{opt}} = k_d^{\mathrm{opt}} L/k_a^{\mathrm{opt}} \equiv g(X)$ is an increasing function of X, such that $2 \equiv \gamma_- < g(X) < \gamma_+ \simeq 5$ for $X < X^*$, so that the parameter L can be chosen close to $2k_a/k_d$. This ensures that $X = g^{-1}(Lk_d/k_a)$ is arbitrarily small and determines the corresponding value of $\omega = 2D_b X^2/L^2$ to tune. Finally, this shows that, in principle, one can *always* determine parameters L and ω such that $K_v^{\mathrm{Pois.}}$ is maximal for (k_a, k_d) while maintaining a small value of X to ensure efficient sorting, and thus define an optimal setup to be used. Furthermore, our approach quantifies the theoretical efficiency of such sorting.

In practice, experimental constraints limit the accessible range of system sizes $(L_{\min}, L_{\max})$ and flow frequencies $(\omega_{\min}, \omega_{\max})$. As an example, for a typical microfluidics setup, these ranges are of the order of $(10\ \mu m, 1\ mm)$ and $(0\ s^{-1}, 10\ s^{-1})$, respectively. Several cases have then to be considered: (i) For species such that $L_{\min} k_d/k_a < \gamma_- < L_{\max} k_d/k_a$, the optimal setup for efficient sorting defined above is indeed realizable and the constraint on ω is irrelevant for all values of D_b; (ii) For species such that $\gamma_- < L_{\max} k_d/k_a < \gamma_+$, the maximum sorting efficiency can be reached for $L = L_{\min}$. This implies a corresponding value of $\omega = 2D_b X^2/L_{\min}^2$, which constraints the range of applicable diffusion coefficients D_b to $D_b < \omega_{max} L_{\min}^2/2X^2$. (iii) For species such that $L_{\min} k_d/k_a > \gamma_+$ or $L_{\max} k_d/k_a < \gamma_-$, the method is in practice not applicable.

Microfluidic technology offers a particularly versatile set of tools to taylor the geometry, flows and surface properties to design experimental setups for the measurement of adsorption and desorption rates (stationary case) or separative applications (stationary and oscillatory cases)

according to the predictions of the present work. In practice, for a typical microfluidic channel one has a transverse length $L \sim 10^{-4} - 10^{-3}$ m and velocities up to $\bar{v} \sim 10^{-4} - 10^{-3}$ m.s^{-1}, while colloids, macromolecules and molecular solutes have diffusion coefficients in the range $D_b \sim 10^{-12} - 10^{-9}$ m^2.s^{-1}. Oscillatory flows can be considered of the form $v(\mathbf{y}) \cos \omega t$ if momentum diffusion in the direction transverse to the flow is fast compared to the period of the flow, i.e. $\omega \ll L^2/\nu$ with ν the kinematic viscosity of the fluid. Such a condition is always satisfied for water in a microfluidic channel, given that $\nu_{\mathrm{H2O}} \sim 10^{-6}$ m^2.s^{-1} and that only frequencies smaller than $\omega/2\pi \leq 1$ s^{-1} can be achieved. This last point also indicates that the present approach will allow to measure sorption/reaction rates slower than 1 s^{-1}. As an example, the dissociation rate of DNA double-strands, which depends on the number of base pairs (bp), can be in the range $10^{-5} - 10^{-3}$ s^{-1} for a few tens of bp [23–25]. If one considers a surface grafted with single-strand DNA, one could selectively separate from a solution a strand containing the complementary sequence by adjusting the flow period and the grafting density in order to tune the adsorption rate k_a (in the low surface coverage limit, it will be proportional to the latter).

VI. CONCLUSION

In conclusion, the present study introduces general analytical results which extend previous works on Taylor diffusion without adsorption and desorption or on a 0-dimensional two-state model valid only in the perfectly stirred limit. This approach is not limited to the Poiseuille flows considered here as an illustration. In particular, it can be straightforwardly extended to the case of electro-osmotic flows, in which an additional length scale, the Debye screening length, can be tuned by changing the ionic strength of the solution. The now well-established microfluidic and rising nanofluidic technologies offer a particularly versatile set of tools to taylor the geometry, flows and surface properties to design experimental setups for the measurement of adsorption and desorption rates (stationary case) or separative applications (stationary and oscillatory cases) according to the predictions of the present work.

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